

M-BDC (M = Co and/ or Fe) MOFs as effective catalysts for hydrogen generation via hydrolysis of sodium borohydride

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Abstract Mono- (Co-BDC, Fe-BDC) and bimetallic FeCo-BDC Metal-Organic Frameworks are successfully synthesized by the solvothermal method in DMF at 150 °C within 15 h and tested as catalysts for sodium borohydride hydrolysis. The materials are characterized by FTIR, PXRD, TGA, ICP-OES, H₂-TPR, BET model, and SEM-EDS. The catalytic activity of these materials is studied for dehydrogenation of sodium borohydride in water at various temperatures under basic conditions. Among tested catalysts, the most promising is Co-BDC, which provides hydrogen generation with a good rate of 1886.8 mL min⁻¹ g_{cat}⁻¹ at 319 K and high efficiency (77.7 %) in the presence of a base. The activation energy determined as 25.4 kJ mol⁻¹ is lower than most cobalt-bearing catalysts for NaBH₄ hydrolysis described in the literature. The catalyst can be reused at least ten times, keeping a good overall hydrogen generation yield, and thus can be considered a promising candidate for portable hydrogen fuel systems.

Keywords: hydrogen generation, Co- and Fe-based catalysts, sodium borohydride, chemical hydrogen storage, Metal-Organic Frameworks

1. Introduction

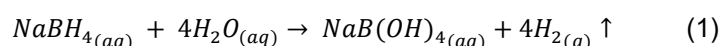
In fast-developing societies, the demand for electric energy is constantly growing. Nowadays, most global energy production is still based on fossil fuels, which resources are depleting, and their

processing involves environmental pollution [1]. Undoubtedly, energy production from renewable resources needs to be expanded and increasingly widespread, with a shift towards green and sustainable energy sources. This shift is essential to reduce greenhouse gas emissions and, associated with them, climate change. Thus, new methods of energy obtainment are searched, in which ecological, technological, and economic issues are crucial. One of the most promising technologies is using hydrogen as an energy carrier. Its high energy per mass content (142 MJ kg^{-1}) and environmentally friendly combustion, upon which only water is generated, are the reasons for intensive research on green, safe, and economical hydrogen production [2] and storage [3]. Due to the Paris Agreement signed in 2015, many countries worldwide have created strategies for hydrogen utilization in energy, transport, and industry [4].

In the transportation sector, hydrogen-powered fuel cell vehicles (FCVs) are becoming more and more important as, together with battery electric vehicles (BEVs), they offer a zero-emission system [3]. At the same time, their refueling time is much shorter than for BEVs (around 10 minutes instead of several hours) [5]. The cells are also promising in smaller-scale portable electronic devices (such as smartphones, laptops, or military equipment) due to their durability and simple design [6]. However, the limiting step for worldwide commercialization of this technology is efficient, safe, and profitable hydrogen storage [7]. Due to the low density of hydrogen (0.09 kg m^{-3} at 273 K), compression (20 - 70 MPa depending on the type of the pressure vessels), cooling (38 K), or their combination are required to obtain useful quantities for on-board applications [2]. Both these technologies are the most mature; however, concerns about their safety, high energy consumption, and costs arise. Thus, the alternative methods involving the physical sorption of molecular hydrogen on porous materials (e.g., zeolite) [8] and the chemical storage in hydrogen-rich compounds, such as metal hydrides, boron-based materials [9], and liquid organic hydrogen carriers (LOHC) are intensively investigated. In chemical storage options, hydrogen can be bounded to a metallic center [10] or non-metallic elements, such as nitrogen [11], boron [12], or carbon (being a part of an aromatic ring) [13]. In this form, it can be stored safely and released on demand via carrier dehydrogenation [14].

Boron-based materials such as borohydrides (e.g., LiBH_4 and NaBH_4) and ammonia borane (NH_3BH_3) are very promising compounds as chemical hydrogen storage materials because of their high hydrogen capacities [15]. Among the borohydrides, sodium borohydride (NaBH_4) has been considered a desirable hydrogen carrier for portable hydrogen storage applications due to its high hydrogen content (theoretically: 10.7 wt%), security, and stability in water [16]. Aqueous alkaline sodium borohydride solutions have become attractive for liquid hydrogen storage, particularly for low-temperature fuel cell applications.

NaBH_4 reacts with water spontaneously; thus, a base (e.g., NaOH) is used to ensure the stability of the solution during storage [17]. The solution can liberate hydrogen effectively at room temperature in the presence of catalysts via the following reaction:



Guella et al. [18] carried out the reaction of NaBH_4 and its deuterated analog NaBD_4 with H_2O , D_2O , and $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures. According to results, in produced hydrogen, half of the equivalents come from BH_4^- anions and half from water, which was proven by the presence of deuterium atoms in the product. In the hydrolysis, only hydrogen is released as a gaseous product; thus, final material purification is not required. The second product – sodium metaborate, is non-toxic and can be recycled to the respective borohydride [19].

The hydrogen production via NaBH_4 hydrolysis is kinetically difficult under ambient conditions without a catalyst [17]. Thus, many efforts have been put into developing active catalysts to ensure a high hydrogen production rate under mild conditions [20–22]. In this regard, noble metal-based materials (especially with Ru [23] and Pt [24]) are particularly effective. Recently, Yang et al. [25] described Ru nanoparticles (NPs) immobilized on Co Al layered double hydroxide, which provided hydrogen generation with a high rate of $44340 \text{ mL min}^{-1} \text{ g}_{\text{Ru}}^{-1}$. The ordered mesoporous silica-supported Pd NPs stabilized by PEG and imidazolium ionic liquid catalyzed NaBH_4 hydrolysis with an activation energy of 35.7 kJ mol^{-1} [22]. The material could be reused five times, ensuring satisfactory conversion. However, due to their scarcity and high price, large-scale utilization of these catalysts is rather limited. Therefore,

non-precious metal-based materials are a desirable alternative, among which cobalt [17], nickel [26], and iron [27] bearing catalysts are the most promising. For example, Bu et al. [28] described Co NPs supported on bagasse-derived porous carbon, which exhibited high activity in hydrogen generation ($11086.4 \text{ mL min}^{-1} \text{ g}_{\text{Co}}^{-1}$ at 298 K) and a relatively low activation energy of 35.2 kJ mol^{-1} . A microporous cryogel p(SPM)-Co system ensured NaBH_4 hydrolysis in seawater, showing an HGR value (Hydrogen Generation Rate) of $1288 \text{ mL min}^{-1} \text{ g}_{\text{Co}}^{-1}$ at 303 K [29].

Although catalysts based on metals like Fe, Cu, Co, and Ni are more cost-efficient, they often suffer from lower catalytic activity compared to noble metals and insufficient stability over the long term. To overcome these problems, two different processes can be adopted: increasing the catalyst surface area and active zone; and producing catalysts with more than one metal in their structure to combine the catalytic capabilities of respective metals in the active site [25,30]. The heterogeneous bimetallic catalysts often exhibit superior catalytic properties to their monometallic counterpart [31]. Frequently, cooperative and synergetic interactions between the two metals are observed due to structural and electronic tuning, which may result in enhanced adsorption and stabilization of intermediates and, thus, higher catalytic activity [32]. The FeCo-B catalyst described by Balbay et al. [33] showed better catalytic activity towards NaBH_4 dehydrogenation than analogous Co-B material (4536 vs. $1869 \text{ mL min}^{-1} \text{ g}_{\text{cat}}^{-1}$). According to the authors, Fe in this system acts as a promoter, which avoids the agglomeration of active sites. Şahin et al. [34] investigated the effect of bimetallic CoFe-based catalyst composition on catalytic properties. The material with a Co: Fe ratio of 4:1 showed better activity than its monometallic counterparts.

As presented above, many catalysts described for NaBH_4 dehydrogenation have a form of metal particles incorporated in a solid support [30,35]. This approach often ensures better mechanical and thermal stability, suppresses active site agglomeration, and facilitates reactant sorption. However, the obtainment of such catalysts requires several steps, including metal precursor incorporation onto a support and subsequent reduction of the precursor. A more straightforward solution is using Metal-Organic Frameworks (MOFs), which recently proved to be a promising class of catalysts for NaBH_4 dehydrogenation. In general, they are hybrid crystalline materials composed of inorganic and organic units. In these compounds, the inorganic components, ions, or metal clusters are connected through polydentate organic linkers, giving rise to porous frameworks that extend in two or three dimensions [36]. They can be obtained by various routes, such as solvothermal [37] and electrochemical [38]. Due to their porous structure and usually large surface area, they facilitate a surface reaction ensuring effective mass transfer. Metallic nodes uniformly distributed in the framework can serve as active sites, whereas the functional groups in organic linkers may take part in the adsorption of reactants. Li et al. [39] described the application of ZIF-9 in hydrogen generation via NaBH_4 hydrolysis. The HGR value determined at 313 K was $3641.69 \text{ mL min}^{-1} \text{ g}_{\text{Co}}^{-1}$. Copper terephthalate (CuBDC) ensured hydrogen release with HGR equal to $7620 \text{ mL min}^{-1} \text{ g}_{\text{cat}}^{-1}$ at 298 K. Iqbal et al. [40] tested the activity of mono- (Fe and Co) and bimetallic (CoFe- NH_2BDC) MOFs at 353 K. The most effective material was the bimetallic catalyst showing a high HGR value ($67000 \text{ mL min}^{-1} \text{ g}_{\text{cat}}^{-1}$) and low activation energy (27 kJ mol^{-1}). Although the reported results are interesting, pure MOFs are not yet widely investigated as catalysts in NaBH_4 hydrolysis.

Taking the above into account, we decided to obtain mono- and bimetallic MOFs based on terephthalates and inexpensive, non-noble cobalt and iron ions by the one-step solvothermal method and test them as catalysts in sodium borohydride dehydrogenation. In general, M-BDCs, depending on the synthetic procedure, form diverse two- or three-dimensional well-organized crystal structures characterized by relatively high specific surface area, which ensures their successful applications as material sensors, catalysts, sorbents, and others [41–43]. MOFs composed of cobalt and/or iron terephthalate, having diverse crystal structures, have already been described in the literature. The Co-based MOF was tested as an anode in Li-ion cells [44]. For the Fe-derived material, sorption properties towards carbon dioxide [45] and methylene blue [46] were described. The bimetallic system was investigated as a catalyst for phenol degradation [47]. However, to the best of our knowledge, the materials with the same structure as described here have not yet been studied as catalysts for the hydrolysis of sodium borohydride. Thus, in this work, for the first time, the influence of the catalyst composition, mass, and temperature of sodium borohydride hydrolysis on hydrogen generation rate (HGR) was evaluated. As till now, only few MOFs were tested in this area, this work may be a next step in developing an active, durable, and cost-efficient catalyst for the dehydrogenation process.

2. Experimental

2.1 Materials and methods

All chemicals were purchased from commercial sources and used without further purification. Cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$), iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$), sodium borohydride (NaBH_4) (98 %), and terephthalic acid (1,4- H_2BDC) (98 %), were acquired from Sigma Aldrich. *N,N*-dimethylformamide (DMF), methanol (MeOH), and sodium hydroxide were purchased from Dinâmica. In the synthesis of the catalysts, a TECNAL TE-016/100 autoclave was used. The FTIR spectra of the reagents and obtained products were recorded on a Bruker Vertex 70/v spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. Powder X-ray diffraction patterns were recorded on a Bruker D2 Phaser using $\text{CuK}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation with Ni filter at voltage 30 kV and 10 mA. Diffractograms were acquired at 2θ values ranging from 5 to 50 ° with a step of 0.02 °. The crystallite sizes of samples were estimated using the Scherrer equation [48], considering the two most intense peaks of the PXRD patterns at around $2\theta = 8.9^\circ$ and 17.8° . The simulated PXRD pattern was obtained using the program Mercury 3.8 and the respective crystallographic data. The SEM images were taken on a high-resolution Mira3 Tescan equipment, with an acceleration voltage of 15 kV, coupled to an Oxford EDS spectrometer. The TG curves were obtained in the temperature range of 30 °C – 900 °C, at a heating rate of 10 °C/min under compressed air, with an airflow of 100 mL min^{-1} , using a thermo-balance model TGA 50 from Shimadzu brand DTG-60H. The content of metallic centers in obtained catalysts was determined by ICP-OES (a Thermo Fisher Scientific spectrometer, model iCAP 6300 Duo, with an axial and radial view and simultaneous detector CID (Charge Injection Device)). ICP experiments parameters were as follows 1150 W radio frequency source power, number of replicas equal to 3, nebulizer, and auxiliary gas flow (0.5 L min^{-1}). The samples were digested in nitric acid (40 mL), and the wavelengths used for each element analyzed in the ICP were 259.8 nm (Fe) and 228.6 nm (Co). The specific surface areas (BET) were measured using N_2 adsorption–desorption isotherms (at 77.3 K) by employing an ASAP2000 surface area analyzer (Micrometric, UK). The pore size distribution was evaluated using the BJH (Barrett, Joyner, and Halenda) model. The samples were degassed at 100 °C under a vacuum for 3 h. All the graphs were analyzed using the software Nova Win 2. The temperature-programmed reduction (TPR) experiments were carried out in a MicrometricsPID ICCS (In situ Catalyst Characterization System) apparatus equipped with a thermal conductivity detector (TCD). The samples (around 80 mg) were placed in a quartz reactor and analyzed in the range of 50 – 300 °C using a 10% H_2/Ar mixture flow (50 mL min^{-1}) at a heating rate of 10 °C/min.

2.2 Catalysts preparation

The mono- and bimetallic MOFs were obtained by the solvothermal method according to the procedure described in the literature [49], with some modifications. To obtain monometallic materials, 3.92 mmol (1.58 g) of $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ or 3.92 mmol (1.14 g) $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ were dissolved in DMF (10 mL). In the case of the bimetallic catalyst, an excess of cobalt salt was applied (Fe:Co molar ratio 1:3), using 3.92 (1.58 g) mmol of $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ and 11.7 mmol (3.40 g) of $\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$. To the salt solution, 1,4- H_2BDC (3.92 mmol; 0.6512 g) dissolved in DMF (10 mL) was added slowly. The solution was transferred to a Teflon reactor coated with stainless steel and left under stirring for 10 min. Then, the reactor was closed and taken to an autoclave, where the reaction was carried out at 423 K for 15h. The resulting product was filtered and washed using DMF and methanol. Then the material was dried under a vacuum at a temperature of 333 K for 6 h. After drying, the final product was obtained: Fe-BDC (0.690 g, dark red powder), Co-BDC (0.490 g, pink powder), and FeCo-BDC (1.0 g, dark brown powder).

2.3 Hydrogen generation experiments

The H₂ generation experiments were carried out at 299, 309, and 319 K in triplicate, using the typical water displacement method [50]. The tests were conducted in the presence of and without sodium hydroxide to determine the base influence on hydrogen release upon hydrolysis.

In a typical experiment, NaBH₄ (40 mg) and an appropriate amount of NaOH (0, 5, 10, or 20 mg) were added to a two-mouthed flask with 10 mL of distilled water. After that, the system was stirred for a few seconds, and the catalyst (5, 10, or 20 mg) was introduced. The displaced volume of water present in an inverted burette was checked and treated as the volume of the produced hydrogen. In addition, blank analyses (without the catalyst) were performed at all temperatures to evaluate the self-hydrolysis of sodium borohydride. In these experiments, NaBH₄ (40 mg) was added to a two-mouthed flask with 10 mL of distilled water, without the catalyst. After that, the system was stirred for a few seconds, and the amount of hydrogen produced was quantified.

The reusability of the most promising catalyst was determined by performing a set of experiments with the catalyst (20 mg) and aqueous solution (10 mL) containing NaBH₄ (40 mg) and NaOH (20 mg). After the hydrolytic reaction, the solution was poured away while the catalyst remained inside the flask. Subsequently, without catalyst regeneration, a fresh portion of NaBH₄, NaOH, and distilled water was added, and the activity of the reused catalyst was determined. These analyses were also conducted without the base.

3. Results and discussion

3.1 Synthesis

The MOF catalysts were obtained by a simple solvothermal method, in which DMF was used as a solvent. The mono- and bimetallic systems were synthesized by reacting cobalt(II) nitrate and/or iron(III) nitrate with 1,4-H₂BDC. The procedure was adapted from the work of Han et al. [49] with some modifications. The authors synthesized CoFe-NH₂BDC materials with different Co and Fe molar ratios and tested them as electrocatalysts for the oxygen evolution reaction (OER). As the highest activity in the OER had the catalysts with a Co: Fe ratio of 3:1, we decided to obtain the bimetallic FeCo-BDC with the same proportions. Although the catalytic reaction was different than described here, we decided to check how this Co: Fe ratio influences hydrogen generation via NaBH₄ hydrolysis. The products were obtained with satisfactory yields, calculated based on the limiting reagent (terephthalic acid): 43.6, 42.9, and 63.1 % for the Fe-BDC, Co-BDC, and FeCo-BDC samples, respectively.

3.2 Catalysts characterization

FTIR

The FTIR spectra of the prepared samples compared to the spectrum of terephthalic acid 1,4-H₂BDC are shown in Figure 1.

The absence of bands in 1680 cm⁻¹ indicates the complete deprotonation of COOH groups and the coordination of the carboxylate groups to the cobalt and iron centers in the synthesized materials. Strong bands in the range of 1590 - 1360 cm⁻¹ correspond to the stretching vibrations (asymmetric (ν_{as}) and symmetric (ν_s) modes, respectively) of COO⁻ in the Co- and/or Fe-based samples. However, in Fe-BDC, the difference in the position between ν_{as} and ν_s is smaller than in the case of Co-bearing materials, which may suggest a chelating coordination mode of the carboxylate groups [51].

Moreover, the band observed at around 550 cm⁻¹ suggests the presence of a desirable Fe-O bond in the material [52]. The narrow band around 3600 cm⁻¹ evident in the spectra of Co-BDC and FeCo-BDC samples is attributed to the bridging O-H groups that link the metallic clusters in the crystal lattice. The FTIR spectra of the Co-BDC and FeCo-BDC materials are practically identical to those previously reported [49].

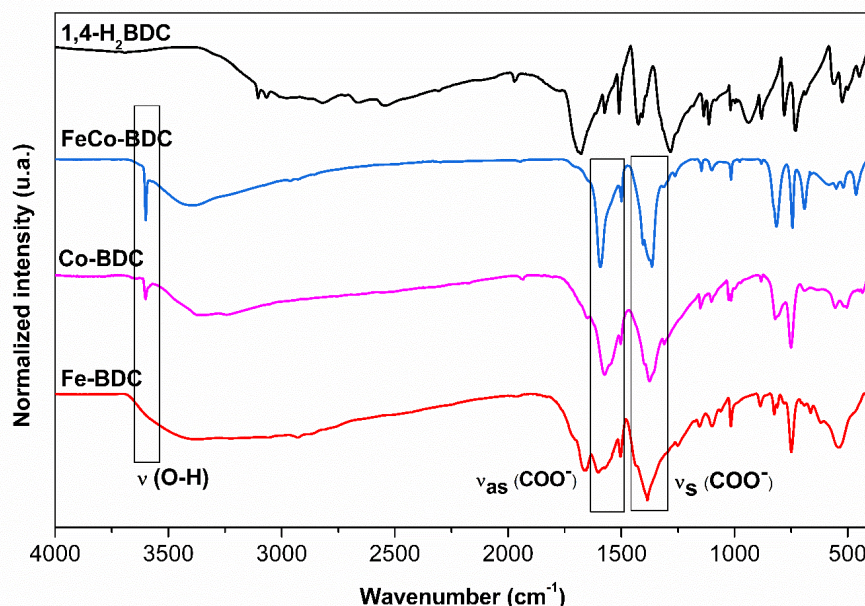


Fig. 1. FTIR spectra of the prepared samples Fe-BDC, Co-BDC, FeCo-BDC, and the pure ligand (1,4-H₂BDC).

PXRD

The PXRD patterns of the samples Co-BDC and FeCo-BDC match well with the simulated pattern of [Co₂(OH)₂1,4-BDC]_n [49], and no additional peaks are observed, which confirms the formation of pure phase products (Fig. 2). The main diffraction peaks at 8.93, 14.10, 15.94, and 17.85 ° are sharp with a high signal-to-noise ratio, indicating good sample crystallinity. The crystal structure of [Co₂(OH)₂1,4-BDC]_n, described in the literature, reveals that cobalt ions are octahedrally coordinated by six oxygen atoms from carboxylic groups of terephthalic anions via bidentate bridging mode and by OH groups [53] (Fig. S1). The crystal structure of the Fe-BDC sample could not be properly identified. The crystalline phase identification of MOFs based on iron and 1,4-H₂BDC is often challenging. They can crystallize in different forms depending on the synthetic conditions (time, temperature, solvent polarity, etc.). Furthermore, they can undergo reversible structural deformations, known as the “breathing” effect, after the adsorption or desorption of guest molecules. These structural transitions provoke significant changes in the XRD patterns, making it difficult or impossible to identify the crystalline phases correctly. It is worth noting the presence of diffraction peaks at around 33.1 and 35.7° assigned to hematite (Fe₂O₃).

Using the Scherrer method [48], the average crystallite size of the samples was determined as 37.01 nm for Fe-BDC, 45.99 nm for Co-BDC, and 31.06 nm for FeCo-BDC. The smaller crystallite size of FeCo-BDC powder is apparently related to the insertion of iron in the material structure.

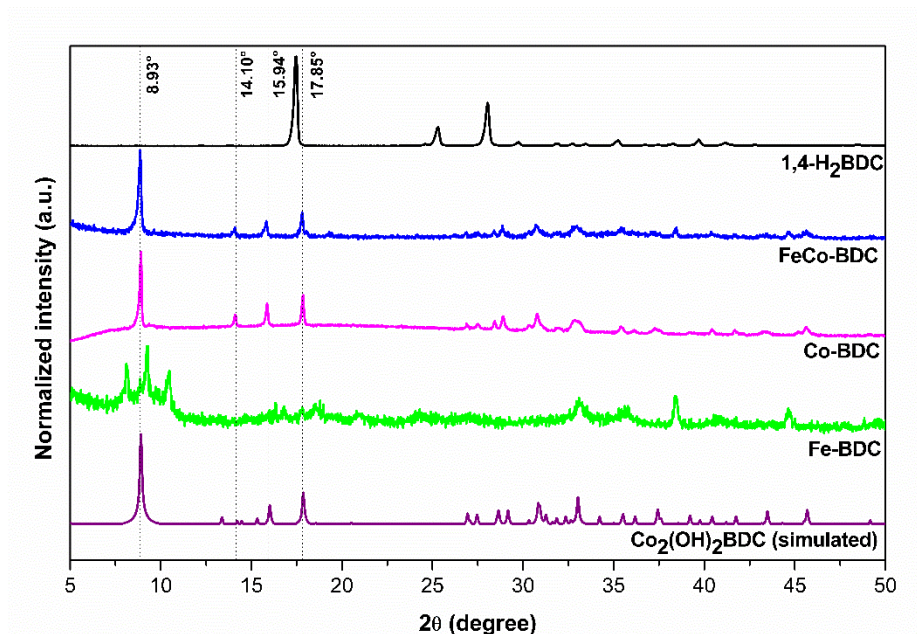


Fig. 2. PXRD patterns of the obtained samples and pure ligand (1,4-H₂BDC) compared to the simulated pattern calculated from the single crystal data of [Co₂(OH)₂1,4-BDC]_n [54] (* diffraction peaks of aluminum support).

SEM

The representative micrographs of MOF samples are shown in Figure 3. The materials occur as agglomerates of various sizes. The Fe-BDC sample is characterized by the biggest particle length (c.a. 28 μm) among analyzed materials. Co-BDC has around ten times smaller particles (average length of c.a. 2.3 μm).

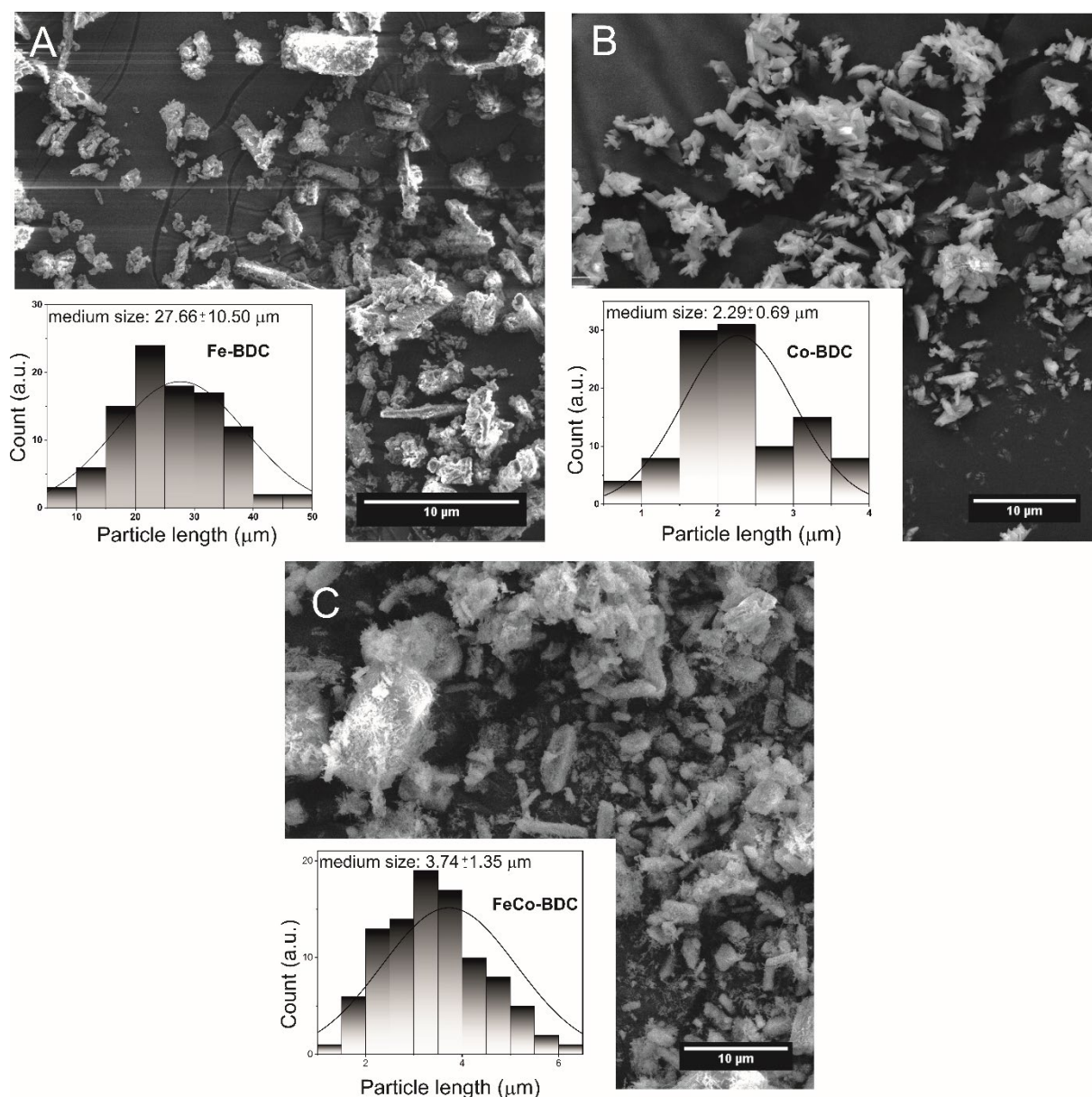


Fig. 3. SEM images and histograms of the particle size distribution of A: Fe-BDC, B: Co-BDC, C: FeCo-BDC.

ICP-OES

To evaluate the metal content in all materials, ICP-OES analyses were carried out (Tab. 1). According to the results, in the Co-BDC sample, the number of metallic sites is only slightly higher than in Fe-BDC. The content is over 1.6-times higher in the bimetallic system than in monometallic samples.

Tab. 1. The content of metals in the catalysts ($m_{\text{cat}} = 20 \text{ mg}$) determined by ICP-OES.

	Fe (mol)	Co (mol)	wt (%)
Fe-BDC	4.44×10^{-5}	—	12.40
Co-BDC	—	4.90×10^{-5}	14.45
FeCo-BDC	1.53×10^{-5}	6.57×10^{-5}	23.61

TGA

The thermal stability of catalysts was determined based on TG analysis (Fig. 4). The thermogravimetric curve of the Fe-BDC material displays a three-step mass loss. The first mass loss event of 7 % observed until 100 °C probably refers to water evaporation. The second mass loss event (14%) observed in a range of 110-270 °C may be ascribed to DMF removal. The third and most significant mass loss starting from 300 °C may correspond to the degradation of coordinated 1,4-BDC molecules (46 %) [44]. The remaining 33 % of the mass comes from Fe₂O₃, formed at 550 °C according to XRD analysis (Fig. S2). Based on the above information and calculation from the TG curve, it can be estimated that the possible chemical formula of Fe-BDC is [Fe₂(OH)₂(DMF)BDC]_n (Tab. S1). These results agree with the ICP results, where a similar content of the metallic species was found for Fe-BDC and Co-BDC samples. In the curve of Co-BDC, the first mass loss of around 12 % may result from the elimination of adsorbed water. The 55 % mass loss observed in the range of 330 – 400 °C probably refers to the thermal degradation of the organic linker. XRD analysis of residue (33 %) obtained after pyrolysis at 550 °C indicates the formation of Co₃O₄ (Fig. S2). For the bimetallic system, the most significant mass loss (25 %) was observed in the range of 330 – 370 °C. It probably refers to organic ligand decomposition. Above 400 °C, no significant mass loss was observed, suggesting complete degradation of the material into metal oxides. The XRD analysis showed the formation of an oxide mixture: CoFe₂O₄ and Co₃O₄. The formation of Fe₃O₄ and Fe₂O₃ is also possible (Fig.S2).

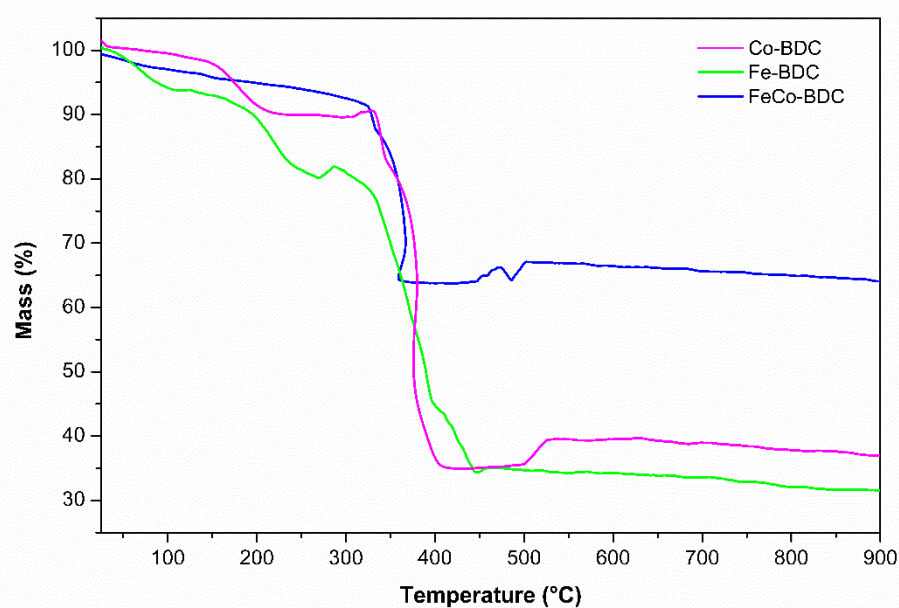


Fig. 4. TGA profiles of the prepared samples (Fe-BDC, Co-BDC, and FeCo-BDC).

BET

The N₂ sorption-desorption curves for studied MOFs are shown in Figure 5. The isotherms obtained for monometallic materials are nearly reversible, and the curves for all samples resemble the II-type isotherm, according to the IUPAC classification [55]. The specific surface areas determined by the BET model for Co-BDC, Fe-BDC, and FeCo-BDC are 16.64, 13.03, and 14.33 m² g⁻¹, respectively. According to BJH analysis, all samples have predominantly mesoporous structures. The Fe-BDC material has the largest pores (average value – 10.31 nm) among analyzed samples, whereas Co-BDC is characterized by the lowest value (Tab. S2). The total pore volume determined from adsorption isotherms for iron-bearing samples is identical – 0.025 cm³ g⁻¹, whereas for Co-BDC, the obtained value is slightly higher (0.031 cm³ g⁻¹).

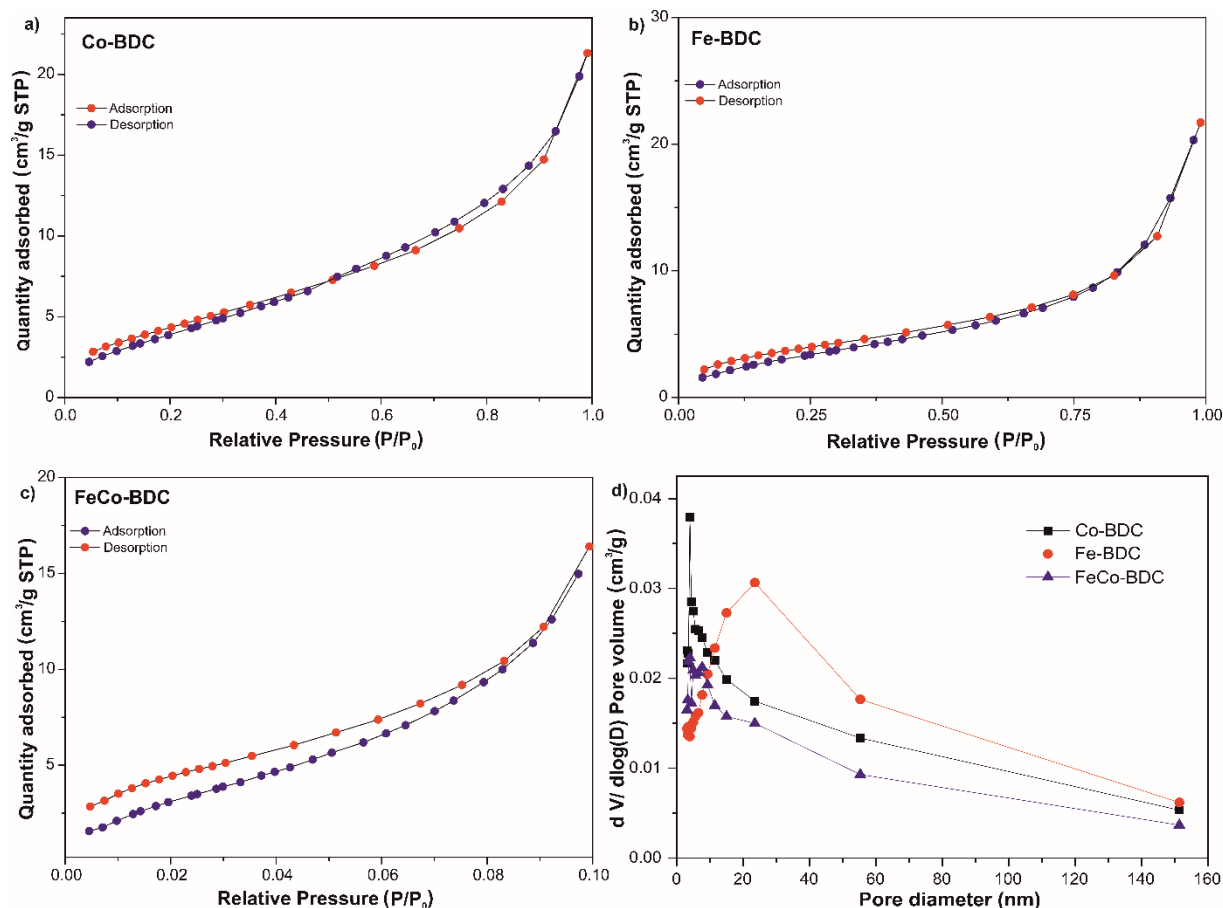


Fig. 5. N₂ adsorption-desorption isotherms obtained for materials: a) Co-BDC, b) Fe-BDC, c) FeCo-BDC; d) BJH pore size distribution from N₂ adsorption isotherm.

H₂-TPR

The reducibility of the samples was studied by the temperature-programmed reduction in H₂ (H₂-TPR). Due to the framework stability determined by TG analysis, the experiments were carried out up to 300 °C. In the monometallic samples, two peaks can be seen in the range of 200 – 300 °C (Fig. 6), indicating the multiple oxidation states of both cobalt and iron (Co²⁺, Co³⁺, Fe²⁺ and Fe³⁺). Lin previously used XANES analysis to confirm the presence of Co²⁺ and Co³⁺ in MOF-74(Co) [56]. Thus, the two steps reduction process implies that Co³⁺ ions are first reduced to Co²⁺ ions and then to Co⁰ at a higher temperature. In a similar way, the reduction of Fe-MOFs involves the conversion of Fe³⁺ ions to Fe²⁺ ions, and then to Fe⁰ [57,58]. According to PXRD analysis, the hematite phase can be present in the Fe-bearing samples. In the presence of hydrogen, it can be transformed into FeO. Thus, broad bands observed in the Fe-BDC profile may result from overlapping several reduction events (i.e., gradual reduction of metallic nods and iron oxides). The TPR profile of FeCo-BDC shows a single reduction peak with a maximum at 279 °C, indicating that there is only one transition from M²⁺ ions to M⁰ ions (M = Co, Fe) in this sample. Additionally, it should be noted that FeCo-BDC may have slightly better reducibility than the bimetallic counterpart.

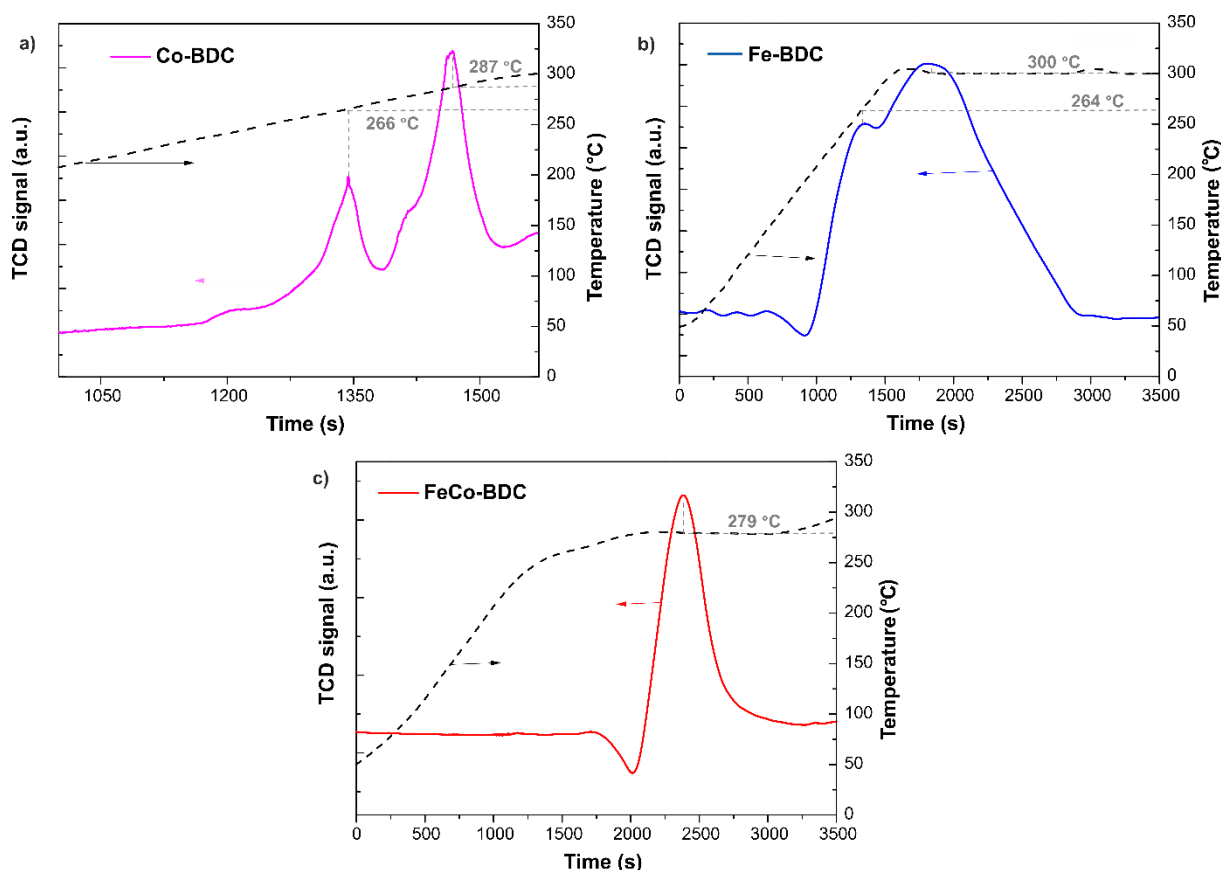


Fig. 6. H₂-TPR profiles of prepared materials: a) Co-BDC, b) Fe-BDC, c) FeCo-BDC (TPR conditions: 10% H₂/Ar mixture flow (50 mL min⁻¹) at a heating rate of 10 °C/min).

3.3 Hydrogen generation

The experiments of hydrogen production via hydrolysis of NaBH₄ were carried out at 299 K, 309 K, and 319 K. In the absence of the catalysts, no gas formation was observed at lower temperatures (299 and 309 K) within 30 minutes of the reaction. Only 10 mL of the hydrogen was produced at the highest temperature during the set time (9.71 % yield) (Fig. S3). The use of the obtained materials as catalysts increased the gas generation significantly (Fig. 7). The best results were obtained using the Co-BDC catalyst, for which 60 mL of H₂ was produced (the reaction efficiency equal to 58.2 %) at near ambient temperature (299 K), while the total reaction time was around 15 minutes. The Fe-BDC sample was the least efficient among the three samples. In this system, 35 mL of hydrogen was generated (efficiency – around 34 %). The reaction efficiency for the bimetallic system was not as good as for the material bearing only cobalt cations (Tab. 2), suggesting that the presence of iron decreases the activity of the catalyst towards hydrogen generation. The analysis of the gas volume changes vs. time showed that the hydrolysis reaction in the presence of the above-mentioned catalysts obeys the zero-order kinetic model (Fig. S4, Tab. S3). The highest rate constant was determined for the Co-BDC-based system.

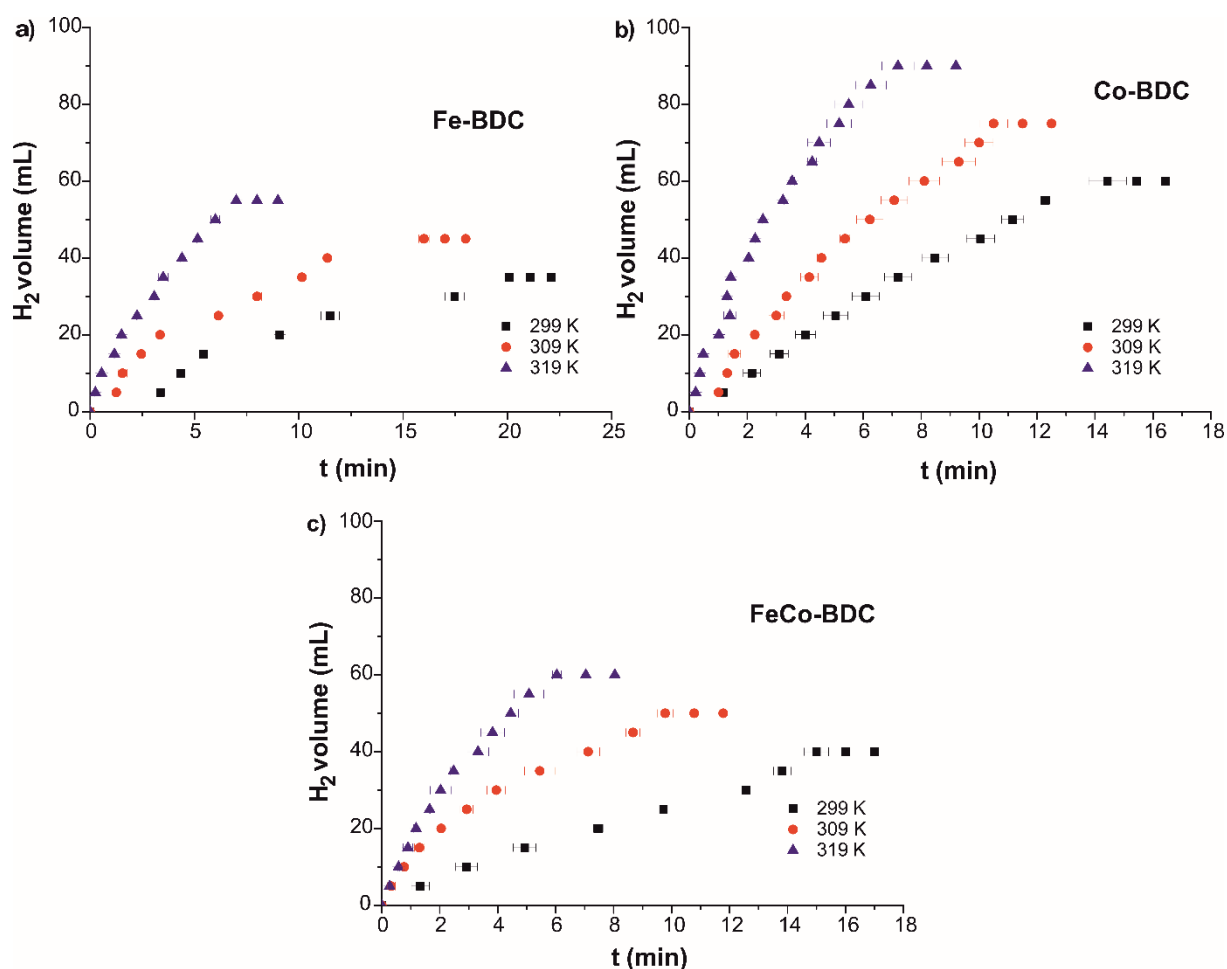


Fig. 7. Hydrogen generation from NaBH_4 hydrolysis catalyzed by a) Fe-BDC, b) Co-BDC, c) FeCo-BDC samples at different temperatures without base (catalyst mass, 20 mg).

Tab. 2. Catalytic performance of Fe-BDC, Co-BDC, and FeCo-BDC in NaBH_4 hydrolysis, without base (catalyst mass, 20 mg).

Catalyst	T (K)	HGR ($\text{mL min}^{-1} \text{g}_{\text{cat}}^{-1}$)	TOF ($\text{mol min}^{-1} \text{mol}_{\text{ms}}^{-1}$)	Efficiency (%)	E_a (kJ mol^{-1})
Fe-BDC	299	87.1	1.6	33.9	59.7
	309	140.6	2.6	43.8	
	319	392.9	7.3	53.6	
Co-BDC	299	208.3	3.5	58.3	43.6
	309	357.1	5.9	72.9	
	319	625.0	10.5	87.6	
FeCo-BDC	299	113.3	1.3	38.9	52.2
	309	275.3	2.8	48.6	
	319	480.8	4.9	58.3	

The increase in temperature positively influences the catalytic performance of all tested materials (Fig. 7, Tab. 2). The most significant effect can be observed for the system with Fe-BDC, in the case of which the increase of temperature by 20 K causes over 4.5 increase in hydrogen generation rate (HGR) value. However, the obtained value at 319 K is still much lower than in the case of Co-BDC under the same conditions. The utilization of the Co-bearing MOF ensures hydrogen generation with good efficiency – over 87 % at the highest temperature. The activation energy of the sodium borohydride hydrolysis catalyzed by Co-BDC was calculated as 43.6 kJ mol⁻¹ (Fig. S5a). This value is lower than the activation energy of other cobalt-based materials, such as Co-B (57.8 kJ mol⁻¹) [59], (65.3 kJ mol⁻¹) [60], Co-B(S) (62.4 kJ mol⁻¹) [61], Co-B@TiO₂ (57.0 kJ mol⁻¹) [21] and Co@C MOF derivative (56.9 kJ mol⁻¹) [20].

To avoid uncontrolled self-hydrolysis, the aqueous solutions of NaBH₄ are stored in the presence of a base [62]. Therefore, a catalyst designed for sodium borohydride hydrolysis should be efficient under basic conditions. To evaluate this, sodium hydroxide was added to the analyzed system. The initial experiments were carried out using the most promising catalyst, Co-BDC. As shown in Fig. 8, even a small amount of the base (5 mg, 0.05 % wt) increases the catalytic performance of the material significantly. At 299 K, the efficiency of hydrogen generation in the presence of NaOH reaches 77.6 % (regardless of the base amount) (Tab. S4). Thus, 20 mg of the base was assessed as an optimum amount and used in subsequent experiments. The addition of NaOH to the bimetallic system also enhances hydrogen production (Fig. S6). However, the effect is not as pronounced as for the Co-BDC sample (Tab. 3). Although the efficiency is the same in both cases, the HGR and TOF values are significantly higher for the reaction with Co-BDC. In the case of hydrolysis catalyzed by Fe-BDC, the presence of NaOH has a negative influence on catalytic performance. Here, almost a two-fold drop in HGR can be observed, followed by a slight decrease in reaction efficiency. Perhaps, it can be connected with the lower stability of the iron-based material under basic conditions. In the FTIR spectrum of the catalyst used in basic NaBH₄ hydrolysis, the changes observed in the carbonyl group stretching bands range may suggest partial decomposition of the coordination polymer (Fig. S7). The positive influence of the base on sodium borohydride hydrolysis was also described for the Co@ZIF-8 catalyst [63]. However, Xie et al. [52] demonstrated an opposite finding when CuO/Cu₃O₄ was used in the reaction.

Similarly, as described before, the hydrolysis under basic conditions obeys the zero-order kinetic model. The determined rate constant *k* for Co-BDC is over five times higher than for the value evaluated without the base (Tab. S3). From the kinetic point of view, basic conditions are not beneficial in the case of the Fe-BDC system – the rate constant decreases almost twice when NaOH is introduced to the reaction mixture.

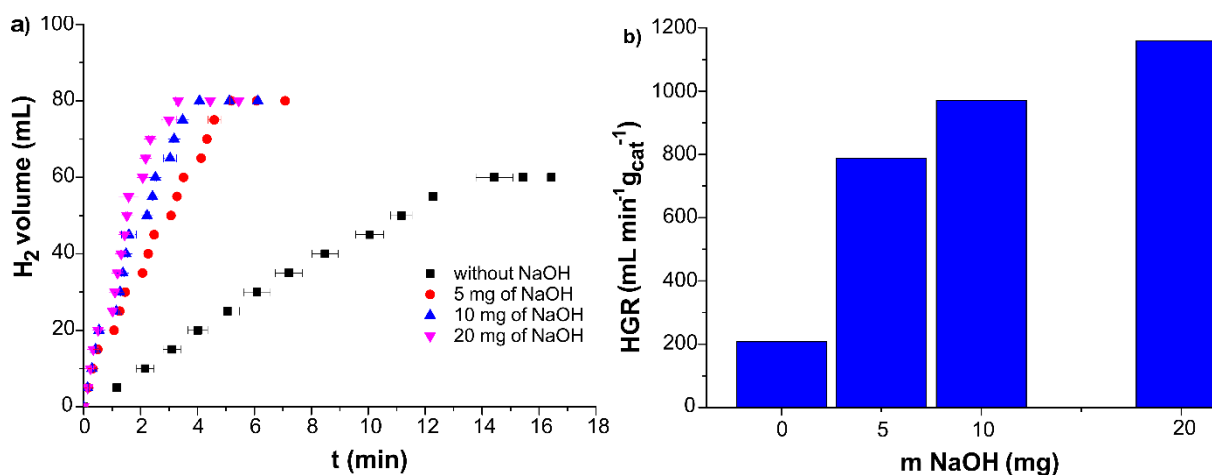


Fig. 8. a) Hydrogen generation from NaBH_4 using Co-BDC as a catalyst in the presence of NaOH; b) the influence of NaOH amount in the system on the hydrogen generation rate (299 K, catalyst mass, 20 mg).

Tab. 3. Catalytic performance of Fe-BDC, Co-BDC, and FeCo-BDC in NaBH_4 hydrolysis in the presence of NaOH (20 mg).

Catalyst	T (K)	HGR	TOF	Efficiency	E_a
		($\text{mL min}^{-1} \text{g}_{\text{cat}}^{-1}$)	($\text{mol min}^{-1} \text{mol}_{\text{s}}^{-1}$)	(%)	(kJ mol^{-1})
Fe-BDC	299	44.0	0.8	29.1	45.3
	309	74.3	1.4	29.1	
	319	147.3	2.7	29.1	
Co-BDC	299	909.1	15.2	77.7	25.4
	309	1194.0	19.9	77.7	
	319	1886.8	31.6	77.7	
FeCo-BDC	299	396.0	4.0	77.7	37.0
	309	793.7	8.0	77.7	
	319	1230.8	12.5	77.7	

The increased temperature causes faster hydrogen generation in the case of all three tested materials (Tab. 3). However, it does not influence the reaction efficiency. For both cobalt-bearing systems (mono- and bimetallic), the highest obtained, under measurement conditions, yield is 77.6 %. The highest HGR and TOF values were determined for the reaction catalyzed by Co-BDC, pointing out that this material is the most efficient under neutral and basic conditions. The presence of the base in the system decreases the activation energy value in the case of all three catalysts. The lowest value was determined for Co-BDC (25.4 kJ mol^{-1}). This value is almost 42% lower than for base-free conditions.

The influence of the catalyst mass on the hydrogen generation in the presence of 20 mg of NaOH is shown in Fig. 9. The increasing amount of Co-BDC has a positive effect on HGR and TOF values. However, it does not increase the reaction yield (77.6 %). The best results were obtained when 20 mg of the catalyst were used ($\text{HGR} = 1731.6 \text{ mL min}^{-1} \text{g}_{\text{cat}}^{-1}$, $\text{TOF} = 28.4 \text{ mol min}^{-1} \text{mol}_{\text{cat}}^{-1}$, at 299 K). According to the results, increasing the amount of catalyst promotes faster gas formation in the system.

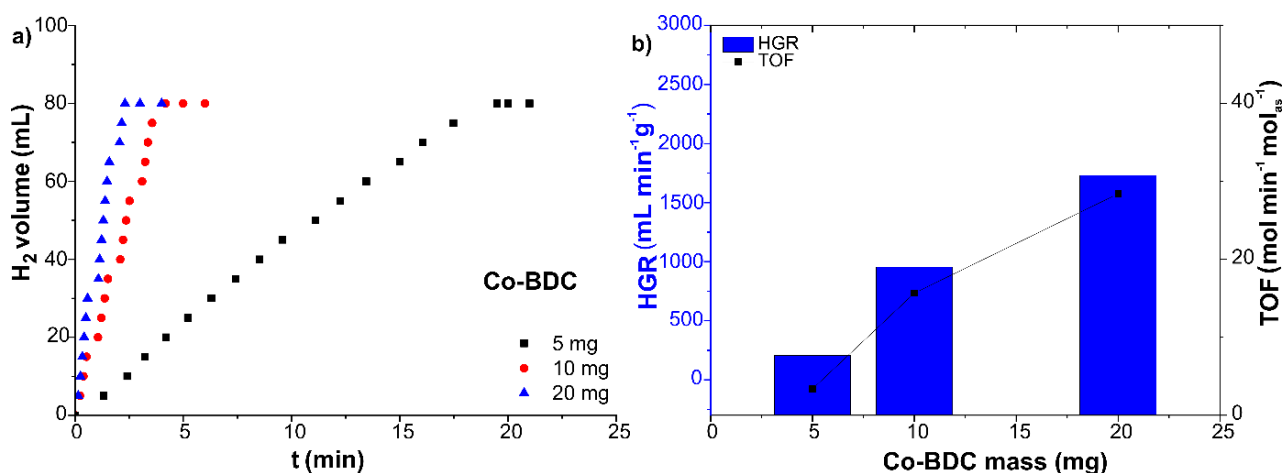


Fig. 9. a) Hydrogen generation from NaBH₄ hydrolysis using different amounts of Co-BDC using 20 mg of the base, at 299 K, b) the influence of Co-BDC mass on HGR and TOF values.

Due to the promising results of hydrogen generation rate and TOF for Co-BDC, this material was selected to evaluate its catalytic stability in cycle analysis at room temperature. The reusability was tested with and without the base (Fig. 10). It is worth pointing out that the catalyst was not regenerated between cycles. According to the obtained results, the NaOH presence has a beneficial effect on both HGR and the durability of the catalytic material. The HGR value determined under basic conditions in the tenth cycle is higher than in the first cycle under neutral conditions. Despite the gradual activity loss, the catalyst shows good performance in all 10 cycles in the presence of the base. The efficiency in the last tested cycle drops to 58.2 % (the initial value is 77.7 %), which is still satisfactory. Experiments carried out without NaOH are characterized by a worse yield of hydrogen generation. In the last, sixth cycle, the value is equal to around 5%, which is over a 10-fold drop in efficiency in comparison with freshly used catalyst.

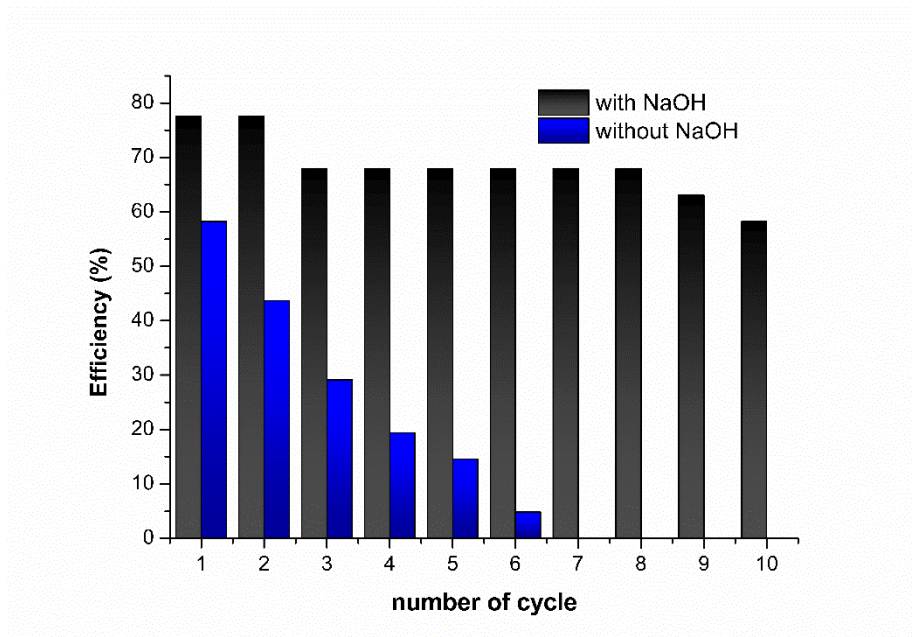


Fig. 10. Reusability of Co-BDC in the presence and without NaOH.

The Co-BDC catalyst shows comparable performance to the results recently described in the literature (Tab. 4). The system is characterized by a higher value of HGR than in the case of MOF-

derived carbon-supported material Co-DABCO-TPA@C-9 [64] and CoB·Ni₄B₃ [65]. For cobalt-based materials obtained after pyrolysis of Co-MOF-71 [66] and supported on colloidal carbon spheres (CCS) [67] and graphene oxide [68], higher values of HGR have been determined; however, these systems are characterized by higher activation energy compared to our materials. Similarly, as the materials reported in the literature, the catalyst can be reused several times, maintaining good efficiency. Even after ten cycles, the material keeps about 75 % of its initial effectiveness.

Tab. 4. Comparison of catalytical performance of some recently reported Co-based catalysts for basic NaBH₄ hydrolysis.

Catalyst	T (K)	Catalyst: NaBH ₄ (mass ratio)	HGR (mL min ⁻¹ g _{cat} ⁻¹)	TOF (mol min ⁻¹ mol _s ⁻¹)	E _a (kJ mol ⁻¹)	Reusability	Ref
Co-DABCO-TPA@C-9	303	2:1	460.06*	11.82	35.09	nd	[64]
CoB·Ni ₄ B ₃	298	1:1.9	500	nd	32.7	5 cycles	[65]
Co@C	303		1680	nd	45	93% after 5 cycles	[66]
Co@C-700	303		291.67*	nd	56.9	93% after 5 cycles	[20]
Co/CCS	295	1:5	1892.86*	23.27*	33.4	nd	[67]
Co/PGO	298	1:4	4066.41*	nd	55.22	73% after 5 cycles	[68]
Co-BDC	319	1:2	1886.8	31.6	25.4	87.5% after 5 cycles	This work

*Calculated based on data presented in articles, nd – not determined

3.4 Post-catalysis characterization of the materials

The analysis of SEM micrographs shows that after the catalytic reaction, the morphology of the materials changed (Fig. S8). The catalysts used in the hydrogen generation process appear as agglomerates of irregular shape. EDS analysis indicates a change of elemental composition on the surface of materials after the catalytic reaction (Tab. 5, Fig S8). The appearance of the sodium atoms after the reaction can be a consequence of sodium metaborate deposition on the surface of the catalysts [62]. The concentration of metallic species in an external layer of the materials (determined for up to 3 μm of depth) increased after the catalytic reaction, suggesting some structural changes upon dehydrogenation. On the other hand, the metal content in a bulk phase determined by ICP-OES decreased (Tab. S5).

Tab. 5. EDS result of synthesized samples before and after their utilization in NaBH₄ hydrolysis.

Catalysts	Fe-BDC	FeH ₂ *	Co-BDC	CoH ₂ *	FeCo-BDC	FeCoH ₂ *
C (wt%)	83.16	6.43	63.06	44.98	80.35	52.2
O (wt%)	15.95	24.06	29.66	21.7	18.20	20.88
Fe (wt%)	0.89	68.6	-	-	1.16	6.14

Co (wt%)	-	-	7.27	32.76	0.29	20.5
Na (wt%)	-	0.91	-	0.56	-	0.27
Total	100	100	100	100	100	100

*FeH₂, CoH₂ and FeCoH₂: samples after hydrogen production.

The XRD patterns of tested materials indicate a lower signal-to-noise ratio and higher FWHM than previously observed for the fresh samples (Fig. S9). The absence of diffraction peaks below 20° in the diffractograms of iron-bearing materials is worth noting. These peaks are usually related to metal-organic structures. On the other hand, in the case of the MOF bearing only cobalt, the diffraction peaks in the range of 8° - 20° are observed even after catalytic reaction, suggesting good stability.

In FTIR spectra of Co-BDC used in NaBH₄ hydrolysis, subtle changes in the region of carboxylic group vibrations can be seen (Fig. S10). The relative intensity of asymmetric and symmetric stretching vibration bands has changed after utilizing the material in the catalytic reaction. The ν_{as} (COO⁻) band was slightly shifted to lower wavenumbers ($\Delta\nu = -13\text{ cm}^{-1}$ for the system with 20 mg of NaOH), while the position of ν_s (COO⁻) band moved to higher wavenumbers ($\Delta\nu = +33\text{ cm}^{-1}$). Additionally, a new, intense band at around 950 cm⁻¹ is seen, which can be attributed to stretching vibrations between boron and oxygen [69]. The observed changes can result from sodium metaborate deposition on the catalyst surface. The presence of metaborate may block active sites, which explains the reduced activity of the catalyst in the recycle analysis.

4. Conclusions

In this study, the synthesis and catalytic performance of three MOFs, namely Co-BDC, Fe-BDC, and FeCo-BDC, were described. The materials were successfully obtained in relatively simple, one-step solvothermal method with good yields. According to PXRD and TG analysis, the materials were formed as pure phase products of the possible crystal structure of $[M_2(OH)_2 1,4\text{-BDC}]_n$ (M = Co and/or Fe). The metal content in the materials was determined as 12.40, 14.45, and 23.61 % wt. for Fe-BDC, Co-BDC, and FeCo-BDC, respectively. The materials showed activity for hydrogen release from aqueous solutions of NaBH₄ at 299 K. The most active proved to be the Co-BDC catalyst, which had the smallest particle size among tested materials. This material was also characterized by the largest specific surface area and the smallest pore diameter among tested here catalysts. The bimetallic material having almost two times higher metal content than its monometallic counterparts, showed worse and comparable catalytic properties to Co-BDC and Fe-BDC, respectively. In the presence of sodium hydroxide, the catalytic performance was increased significantly in the case of cobalt-bearing materials; however, the opposite effect was observed for Fe-BDC catalyzed system. Under these conditions, the highest activity showed again the Co-BDC catalyst. For this system, the hydrogen generation rate was determined as 1886.8 mL min⁻¹ g_{cat}⁻¹, while the reaction efficiency was 77.7 %, at 319 K. The estimated value of activation energy for the reaction carried out in the presence of NaOH (i.e. 25.4 kJ mol⁻¹) is among the lowest values described in the literature so far for the Co-catalyzed hydrolysis of NaBH₄. The catalyst revealed good durability under basic conditions. The material could be reused at least 10 times without regeneration, keeping satisfactory HGR and yield at 299 K. The gradual loss of catalytic activity may result from sodium metaborate deposition on the catalyst surface, which blocks the active sites. Even though the catalyst still shows potential for industrial applications. Good activity, stability, and reusability without the need for regeneration make the material a promising candidate for commercialization. Due to the relatively low price of starting materials – cobalt(II) nitrate and terephthalic acid and uncomplicated synthetic protocol, the catalyst may be obtained commercially, like other MOFs, i.e., HKUST-1 and ZIF-8. The material shows good catalytic performance without a need of additional thermal treatment (such as pyrolysis or calcination), which reduces the total costs of an industrial process compared to i.e. biomass-derived catalysts.

Acknowledgments

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